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INFLUENCE OF TEMPERATURE ON THE QUENCHING OF ACTIVE NITROGEN AT VARIOUS PRESSURES

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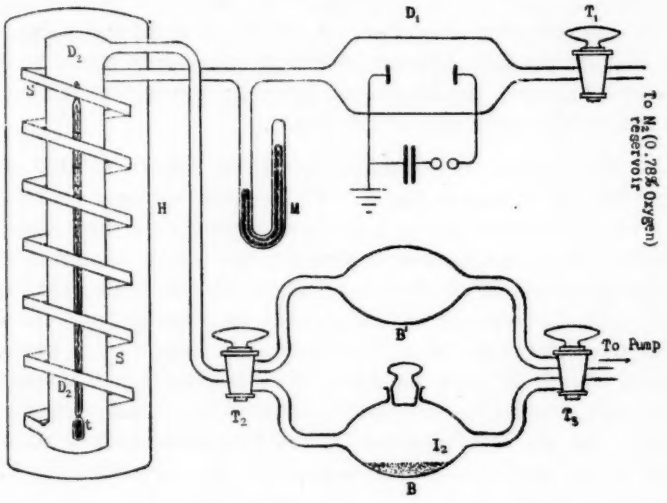
§1. That the after-glow due to active nitrogen is extinguished on streaming the gas through a heated tube was first observed by the present Lord Rayleigh.[1] Jones and Grubb[2] have reported that a greenish yellow glow which appeared intense at $-20°$ C., disappeared on heating to 30° C. Rudy[3] studying the influence of temperature in the range 20–120° C., observed that the corresponding coefficient was much smaller than in ordinary chemical reactions. Results of Cario and Kaplan,[4] Willey,[5] Okubo and Hamada[6] in this line, have raised the interesting question of the nature of the glowless state of active nitrogen obtained by its de-activation by heat or by a weak electrical discharge. A review of these and allied results has shown that the possible influence of the gas pressure in regard to its quenching by heat has been almost entirely ignored; the present work was undertaken to investigate the role of this factor.

§2. The general experimental procedure similar to that adopted in earlier work,[7] is shown in Fig. 1. The cylinder nitrogen containing 0·78% oxygen was activated in D_1, at a pressure shown by the manometer M. The activated gas was then allowed to flow through a long spiral S so as to attain the temperature of the air thermostat H, which was heated electrically from outside. The temperature of the glowing gas issuing from the spiral and entering the wider tube D_2 at its bottom was shown by a thermometer *t*. The two bulbs B, B′ were made as similar as possible; B contained a thin layer of very fine iodine crystals to serve as a sensitive detector of active nitrogen. The gas entering from D_2 could be made to flow through either B or B′ by an appropriate manipulation of the stop-cocks T_2, T_3. Within the range of the flow-rates of the gas which were adjusted by means of T_2, T_3 and suction at T_1, the relative volumes of D_1 and D_2 were such that the after-glow was seen clearly in B or B′. The observation bulbs B and B′ were carefully screened from any extraneous light, so as to enable the

detection of the faintest after-glow by either direct observation in B′ or with the help of the very characteristic bluish white luminiscence excited in iodine by making the gas flow *via* B.[8,7]

The quenching temperature at a given pressure was determined as follows:—At a conveniently low pressure (*cf.* Table I), the gas was allowed to stream through D_1SD_2B'. The discharge tube D_1 was then excited and the heater for the thermostat H started. At a well-defined temperature shown by the thermometer *t* in D_2, it was found that the after-glow in B′ ceases to be observable. The stop-cocks T_2 and T_3 are then quickly manipulated so that the gas flows *via* $D_1S_1D_2B$. It is found that the iodine in B now fails to show the characteristic luminescence. By reducing the heating current, the temperature is allowed to fall slowly. The glow due to the excitation of iodine then soon re-appears in B; the temperature and the pressure, when the iodine glow in B is just perceptible are observed. The heating is once again commenced until the iodine glow is B is undetectable. The mean of these two temperatures is taken as the quenching temperature. It is found that the temperature corresponding to the appearance of the glow on cooling and that for its obliteration on warming at a given streaming



pressure, but seldom differed by more than 1–2° C. The pressure of the activated gas is then slightly raised and the corresponding quenching temperature determined, and so on. These results are shown in Table I.

TABLE I

Press mm. Hg. of streaming gas ..	15	17	20	24	33
Quenching temperature in °C. ..	215	223	236	255	330

§3. Despite investigations by numerous workers, the mechanism of the formation of active nitrogen in the electrical discharge and that of its de-activation is not understood in adequate detail. Evidence based chiefly on the spectroscopy of the after-glow would appear to indicate that besides normal atoms, metastable molecules of 8·2 volts are involved. The occurrence of 2·3 and 3·6 volt metastable atoms has also been postulated. Amongst the several theories for the production of the after-glow, a ternary collision of the following type would appear to summarise most of the facts and has also the advantage of simplicity.[5,12]

$$N + N' + N_2 = 2N_2 + \text{after-glow}$$

where N′ denotes a 2·3 volt metastable atom.

The work of Rayleigh[9] as far back as 1912, Angerer,[10] Bonhoeffer and Kaminsky,[11] Rudy[3] and especially Willey[5,12] has established that kinetically the decay of the after-glow is a 'high order' re-action. The above type of mechanism is in agreement with this finding. It also explains the observed pronounced influence of the gas pressure on the reduction of the duration of the after-glow. The after-glow may be ascribed chiefly to de-activation due to collisions of the second type of the nitrogen atoms and molecules, with the rest of the molecules both in the gas space and on the walls of the containing vessel. The observed general suppressant effect of both heat and rise of the gas pressure may then be attributed to the corresponding increase in the collision frequency. These general considerations are, however, insufficient to explain our finding—which does not appear to have been recorded in the now considerable literature on active nitrogen, that its quenching at a given pressure is characterised by a definite temperature and that furthermore, this quenching temperature increases by increasing the gas pressure. In fact, on general grounds indicated above, it would appear that a rise in gas pressure should correspond to a *decrease* in the quenching temperature. Further work is necessary to elucidate this discrepancy. The quenching temperature being determined by the cessation of the after-glow and the sensibly simultaneous loss of capacity for exciting the iodine luminiscence as the streaming gas is progressively warmed, and by observation of their concomitant reappearance on cooling, suggest that

the above properties, *viz.*, the after-glow and capacity for exciting luminiscence are inseparable. We are of opinion therefore, that the evidence of our observation argues against the existence of a '*dark*' but chemically active form of nitrogen.

Summary

Effect of heating active nitrogen has been investigated at various streaming pressures in the range 15 to 33 mm. Hg by observation of its after-glow visually and excitation of the iodine luminiscence. It is found, it would appear for the first time in this field of research that the quenching of the after-glow is produced at a well-defined temperature, which increases with increase of the gas pressure. Existence of a glowless but chemically active form of nitrogen is considered improbable.

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CHEMICAL EXAMINATION OF THE ROOTS OF *CENTAUREA BEHEN* LINN.

Isolation of Behnin

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Received October 25, 1943

Centaurea Behen or *Centaurea Behman*, commonly known in Hindustani as 'Lal Behman' and 'Rakta Barni' in Bengali, is an annual herb belonging to the Natural Order 'Compositæ'. It is cultivated throughout Northern India for the sake of its highly medicinal roots, which are used as remedial agents in various diseases.

Red Behman is a tuberous root consisting of a central part about 2″ in diameter, from which spring 5 or 6 tapering tubes $1\frac{1}{2}$″ to 2″ long and $\frac{1}{2}$″ to 1″ in diameter. At the top of the central tuber the scaly crown is 2″ in diameter. The external surface of the root is reddish brown and marked by numerous circular and longitudinal wrinkles, but internally there is a dull red woody central portion surrounded by a thick yellowish white horny layer. In the commercial article the root is sliced and the central woody part removed, but it is always associated with the white layer.

Red Behman, the drug of the ancient Persians, was introduced by the Arabs in the West. The drug is considered to be expelling flatulence and aphrodisiac by Dymock, Warden and Hooper.[1] Accordingly these are used in callous affections and jaundice as well as resolvents of phlegmatic humours.

In literature nothing has been mentioned regarding the chemical constituents of this plant. In view of its important medicinal properties however, the present authors have been tempted to put it to a thorough chemical examination in order to have an insight into the nature of its active principle. An account of the active principle of the root is given in this paper. It is indeed amazing that no alkaloid has been found in it as is mentioned by Kirtikar and Basu.[2] Instead, a resinous fatty matter, a saponin and a reddish white crystalline substance of the nature of a $\Delta^{\alpha\beta}$-unsaturated lactone have been isolated in small amounts and analysed. Most probably its medicinal property is due to the latter substance. It has been named 'Behnin', having a molecular formula $C_{24}H_{48}O_3$. Further it is

found to contain a methoxy group according to the determination made by micro-Zeissel's method.

Experimental

For extraction with different solvents, the dry root was crushed to fine powder and extracted in a Soxhlet's extractor in lots of 25 gm. each in order to ascertain the best solvent. The solvent was recovered by distillation in each case and the residue brought to a constant weight by keeping in a steam oven with the following results:—

1. *Alcohol extract* (15·7%).—Brown resinous mass, soluble in benzene but insoluble in water, giving a yellow colour with caustic soda, an intense red colour with concentrated sulphuric acid no precipitate with lead acetate, thus showing the presence of a lactone.

2. *Benzene extract* (10·5%).—Brown waxy residue, soluble in chloroform, insoluble in water, giving a yellow colour with caustic soda and red with strong sulphuric acid.

3. *Ethyl acetate extract* (4·36%).—Red resinous product, soluble in hot alcohol, neutral to litmus, yellow with caustic soda, decolourising bromine water, reducing potassium permanganate and finally giving a dirty green precipitate with ferric chloride.

4. *Chloroform extract* (10·4%).—Brown fatty residue, giving a beautiful yellow colour with alcoholic caustic potash.

5. *Aqueous extract* (23·2%).—A red brittle solid giving froths on heating the aqueous solution, precipitating with lead acetate and reducing Fehling's solution, probably due to sugars and tannins.

The powdered root on complete incineration left 14·85% water-soluble and 85·15% water-insoluble ash. The following radicals were detected:—

(*a*) In the water-soluble portion: SO_4CO_3, Cl, Na and K

(*b*) In the water-insoluble portion: CO_3, Al, Ca and Mg.

For exhaustive extraction 8 kg. of the powdered roots were extracted with alcohol three times, in lots of 2 kg. each, in a 5 litre flask. The extract was filtered hot and allowed to stand overnight, when it gave a buff coloured precipitate. It was filtered and the filtrate was set aside for further examination. The precipitate was washed with alcohol in order to remove the tannin and the colouring matter. On keeping in air, it could not be obtained dry on account of the presence of fatty and resinous matter in it. Hence it was repeatedly washed with petroleum ether to remove the impurities. The product was then extracted with hot alcohol

and animal charcoal a number of times and the solution filtered through a hot water filter funnel. After keeping for some time, the precipitate was filtered through a Buchner funnel under suction, washed with petroleum ether and dried in air. On crystallisation from alcohol slightly red crystalline leaflets, melting at 79·80° C. were obtained.

The previous filtrate already mentioned was distilled to recover the solvent and the residue poured into water to remove the sugars and tannins which were soluble in water It could not be filtered due to the formation of an emulsion. Hence it was allowed to stand for two days, treated with common salt and heated in a beaker. On cooling, a slightly red precipitate was formed. It was filtered, dissolved in alcoholic caustic soda and precipitated with dilute sulphuric acid. This precipitate was filtered, washed with alcohol and dried in air. The above filtrates were combined and examined later on. On crystallisation of the precipitate alternately from benzene and methyl alcohol with the addition of animal charcoal crystalline leaflets sintering at 72° C. and melting at 79-80° C. were obtained. The whole operation was tedious and involved tremendous difficulties.

From the combined filtrates mentioned above a saponin was isolated but it was insufficient for further examination.

Properties.—It is a light buff coloured crystalline substance. It is soluble in chloroform, sparingly soluble in ethyl alcohol, benzene and methyl alcohol and insoluble in water. On boiling with water for a long time, it melts to an oily liquid which on cooling becomes resinous and greasy probably due to decomposition. When heated quickly, it decomposes completely with the evolution of black fumes and a luminous flame. On exposure to ordinary sun light, behnin assumes a yellow colour, but in strong direct sun light it is converted into a sticky yellow resin. It is insoluble in 5% aqueous caustic soda solution but on heating it dissolves slowly with a yellow colour. It develops an intense beautiful yellow colour with alcoholic caustic potash as in the case of $\Delta^{\alpha\beta}$-unsaturated lactones studied first by Thiele[3] and subsequently by Jacobs and Hoffmann.[4]

In strong sulphuric acid, it produces a red colour. It decolourises a solution of bromine in chloroform and a dilute alkaline solution of potassium permanganate. It does not give any colour with ferric chloride, nor does it reduce Fehling's solution. It gives a positive Salkowski's reaction producing a red tinge. In Liebermann-Burchard reaction, behnin turns green. It becomes intense yellow in strong nitric acid and gives no precipitate with lead acetate. Behnin gives no colour with an alkaline solution of sodium nitroprusside. It has been found to contain a methoxy group and

forms tetrabromo derivative. It has got no alcoholic hydroxy group, as it does not form any acetyl or benzoyl derivative. Thus both the remaining oxygen atoms account for the lactonic grouping. Results of a series of analyses and molecular weight determinations point to a molecular formula $C_{24}H_{48}O_3$. (Found: C = 75·18, 74·79; H = 12·66, 12·72; M.W. by Rast's camphor method = 372, 378, 408; $C_{24}H_{48}O_3$ requires C = 75·01; H = 12·5%; M.W. = 384.)

Estimation of Methoxyl Group.—The determination was conducted by the micro-Zeissel's method. (Found: OCH_3 = 7·94; $C_{23}H_{45}O_2$ (OCH_3) requires OCH_3 = 8·07%.)

Tetrabromo Derivative.—Behnin (0·2 gm.) was dissolved in chloroform (15 c.c.) and treated with a solution of bromine in chloroform. It was allowed to stand in dark for 4 hours and heated on a water-bath under reflux for half an hour. On evaporating the solvent, a semi-solid pasty mass was obtained. It was crystallised from alcohol in yellow needles melting at 67° C. (Found: Br, 45·12; $C_{24}H_{48}O_3Br_4$ requires Br, 45·45%.)

Summary

From the roots of *Centaurea Behen* a crystalline unsaturated lactone having a molecular formula $C_{24}H_{48}O_3$ has been obtained.

It has been found to contain a methoxy group and to yield a tetrabromo derivative.

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ON THE EXISTENCE OF A METRIC FOR HIGHER PATH-SPACES*

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The geometry associated with the system of differential equations

$$\frac{d^{(\sigma+1)}x^i}{dt^{(\sigma+1)}} + F^i(t, x, x', \ldots . x^{(\sigma)}) = 0$$
$$i = 1, 2, \ldots . n \qquad \sigma \geqslant 2$$

has been studied by Kosambi. In this note we investigate the conditions under which the above system of differential equations may be identified with the extremals $\delta \int f dt = 0$. D. R. Davis[1] and D. D. Kosambi[2] for the case $\sigma = 1$ and the present author[3] for $\sigma = 2$ have already established the result that "The necessary and sufficient condition for the differential equations I to be the extremals of a regular problem of the calculus of variations is that the equations of variation of I be self-adjoint." In this note we establish the above result for the general σ.

1. We find that the self-adjoincy conditions imply the existence of a tensor f_{ij} such that

$$\left.\begin{aligned} f_{ij} &= f_{(\lambda)i(\lambda)j}, \qquad \lambda = \frac{\sigma+1}{2} \text{ when } (\sigma+1) \text{ is even,} \\ f_{ij} &= \phi_{i(\lambda)j} - \phi_{j(\lambda)i}, \ \lambda = \frac{\sigma}{2} \text{ when } (\sigma+1) \text{ is odd} \end{aligned}\right\} \quad (1\cdot1)$$

We shall consider for the present the even and odd order cases separately.

Case i $(\sigma + 1)$ *even.*—In this case, the self-adjoincy conditions are merely linear conditions on $f_{(\lambda)i(\lambda)j}$ so that we can add to f, a function ϕ such that

* Read at the Thirteenth Conference of the Indian Mathematical Society held at Annamalainagar (December 1943).

I express my grateful thanks to Prof. D. D. Kosambi for his valuable suggestions.

[1] D. R. Davis, *Bull. Amer. Math. Soc.*, 1929, 371–80.

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$\phi_{(\lambda)i(\lambda)j} = 0$, *i.e.*, $\phi = \phi_r x^{(\lambda)r} + \psi$, where ϕ_r and ψ are functions of $(t, x, x^1, \ldots x^{(n-1)})$ and

$$\delta_i (f + \phi_r x^{(\lambda)r} + \psi) = 0$$

or
$$E_i = \delta_i f = -\delta_i (\phi_r x^{(\lambda)r} + \psi).$$

We can regard this as a differential system for the unknowns ϕ_r and ψ in terms of the known f. The conditions of integrability of this system should be identically satisfied in virtue of the self-adjoincy conditions. Or we can argue thus : The system E_i should be identified with $-\delta_i (\phi_r x^{(\lambda)r} + \psi)$. We *assume* that for this which is a differential system of order σ, the necessary and sufficient condition for the identity to hold good is that the equations of variation of E_i should be self-adjoint. That E_i satisfies this criterion is established in Art. 3. Since the result has been established for $\sigma = 1$ and $\sigma = 2$ it transpires that the theorem is true for the general σ by induction. That is, the existence Theorem is carried over automatically to one order lower at which stage the argument may be repeated.

Case ii $(\sigma + 1)$ *odd.*— In this case, the metric sought must be of the form $f = \phi_r x^{(\lambda)r} + \psi$. The Euler equations assume the form

$$[\phi_{i(\lambda)j} - \phi_{j(\lambda)i}] x^{(\sigma+1)j} + M_i = 0.$$

Since the self-adjoincy conditions imply, in this case, the existence of an $f_{ij} = \phi_{i(\lambda)j} - \phi_{j(\lambda)i}$ we can regard the function ϕ_i in f as known and determined to within a function whose λ-curl vanishes. The addition of such a function to f merely amounts to adding a perfect differential and hence can be ignored. So we now regard $\delta_i (\phi_r x^{(\lambda)r} + \psi) = 0$ as a differential system for the unknown ψ in terms of the known f, or we can argue as in case i.

In both cases we find that the discussion practically reduces to one of the lower order. The only point to be kept in mind is that even and odd orders which alternate in the reduction have a different structure.

2. Self-adjoincy conditions:

It is known[4] that $\underset{(p)}{A_{ij}} u^{(p)j} = 0$ will be self-adjoint if and only if

$$\underset{(p)}{A_{ij}} = \sum_{r=p}^{\sigma+1} (-1)^r \binom{r}{p} \underset{(r)}{A_{ji}}^{(r-p)}, \quad p = 0, 1, \ldots \sigma + 1.$$

Applying these conditions to the equations of variation of

$$H_i (t, x, x', \ldots x^{(\sigma+1)}) = 0 \text{ we get}$$

$$H_{i(p)j} = \sum_{r=p}^{\sigma+1} (-1)^r \binom{r}{p} H_{j(r)i}^{(r-p)} \qquad (2{\cdot}1)$$

[4] D. D. Kosambi, *Quart. J. of. Math.*, 1936, 7, 103.

For $p = \sigma + 1$ we get $H_{i\,(\sigma+1)\,j} = (-1)^{\sigma+1} H_{j\,(\sigma+1)\,i}$ (2·2)

For $p = \sigma$ $H_{i\,(\sigma)\,j} = (-1)^{\sigma} H_{j\,(\sigma)\,i} + (-1)^{\sigma+1}(\sigma+1) H^{(1)}_{j(\sigma+1)i}$ (2·3)

Equating to zero the coefficient of $x^{(\sigma+2)k}$ in the above, we get

$$H_{j\,(\sigma+1)\,i\;(\sigma+1)k} = 0$$

and hence
$$H_i = f_{ij}\, x^{(\sigma+1)j} + M_i \tag{2·4}$$

where f_{ij} and M_i contain $(t, x, x' \ldots x^{(\sigma)})$.

It follows from (2·2) that $f_{ij} = (-1)^{\sigma+1} f_{ji}$, which shows that the tensor of association is symmetric if $(\sigma + 1)$ is even and anti-symmetric when $(\sigma + 1)$ is odd. The condition (2·3) applied to the form (2·4) gives

$$[f_{ik(\sigma)j}\, x^{(\sigma+1)k} + M_{i(\sigma)j}]$$
$$= (-1)^{\sigma}[f_{jk(\sigma)i}\, x^{(\sigma+1)k} + M_{j(\sigma)i}] + (-1)^{\sigma+1}(\sigma+1) f^{(1)}_{ji} \tag{2·5}$$

The co-efficient of $x^{(\sigma+1)k}$ in (2·5) equated to zero gives

$$f_{ik(\sigma)j} + f_{kj(\sigma)i} - (\sigma+1) f_{ij(\sigma)k} = 0$$

Permuting i, j, k cyclically and adding, we get

$$f_{ik(\sigma)j} + f_{ji(\sigma)k} + f_{kj(\sigma)i} = 0$$

and hence
$$f_{ij(\sigma)k} = 0. \tag{2·6}$$

The residual terms in (2·5) give us $Df_{ij} = 0$ (2·7)

For $p = \sigma - 1$ we get

$$[f_{ik(\sigma-1)j}\, x^{(\sigma+1)k} + M_{i(\sigma-1)j}]$$
$$= (-1)^{\sigma-1}[f_{jk(\sigma-1)i}\, x^{(\sigma+1)k} + M_{j(\sigma-1)i}] + (-1)^{\sigma}\binom{\sigma}{\sigma-1} M^{(1)}_{j(\sigma)i}$$
$$+ (-1)^{\sigma+1}\binom{\sigma+1}{\sigma-1} f^{(2)}_{ji}$$

Equating to zero, the coefficient of $x^{(\sigma+1)k}$ in this we get

$$f_{ik(\sigma-1)j} - f_{kj(\sigma-1)i} + (-1)^{\sigma+1}\sigma\, M_{j(\sigma)i(\sigma)k} - \binom{\sigma+1}{2} f_{ij(\sigma-1)k} = 0.$$

Interchange i and k and subtract in the even case and add in the odd case. We get

$$\left.\begin{aligned} f_{ik(\sigma-1)i} - f_{ji(\sigma-1)k} &= 0 \text{ (even case)} \\ \left[\binom{\sigma+1}{2} + 1\right](f_{kj(\sigma-1)i} + f_{ij(\sigma-1)k}) &= (-1)^{\sigma}\cdot 2\sigma\cdot M_{j(\sigma)i(\sigma)k} \\ &\text{(odd case)} \end{aligned}\right\} \tag{2·8}$$

Similarly, equating to zero, the coefficient of the highest derivative of x^k that is present in the other conditions for $p = \sigma - 2, \sigma - 3, \ldots . 1, 0$ we get

$$\left.\begin{aligned}\binom{\sigma-1}{p} f_{jk(\sigma-1)i} - \binom{\sigma}{p} \mathrm{M}_{j(\sigma)i(\sigma)k} + \binom{\sigma+1}{p} f_{ji(\sigma-1)k} = 0 \\ p = \sigma-2,\ \sigma-3, \ldots . 1, 0\end{aligned}\right\} \quad (2\cdot9)$$

In the even case (2·8) can be derived from (2·9). So that (2·9) constitute a set of $(\sigma-1)$ simultaneous homogeneous linear equations in the three unknowns $f_{jk(\sigma-1)i}$, $\mathrm{M}_{j(\sigma)i(\sigma)k}$, $f_{ji(\sigma-1)k}$ and hence they vanish if $\sigma-1 \geqslant 3$, *i.e.*, $\sigma+1 \geqslant 6$. In the odd case there are σ such equations and hence they vanish if $\sigma \geqslant 3$, *i.e.*, if $\sigma+1 \geqslant 5$. It is easily verified that the matrix of the coefficients is of the required rank 3. Hence we have,

$$f_{ij(\sigma-1)k} = 0,\ \mathrm{M}_{i(\sigma)j(\sigma)k} = 0 \quad (2\cdot10)$$

Using the results (2·10) let us equate to zero, the coefficients of the next highest derivative of λ^k that is present in these conditions. We get for $p = \sigma-2$,

$$f_{ik(\sigma-2)j} + (-1)^\sigma \left[f_{jk(\sigma-2)i} - \binom{\sigma-1}{\sigma-2} \mathrm{M}_{j(\sigma-1)i(\sigma)k} + \binom{\sigma}{\sigma-2} \mathrm{M}_{j(\sigma)i(\sigma-1)k} - \binom{\sigma+1}{\sigma-2} f_{ji(\sigma-2)k} \right] = 0.$$

Interchange i and k and subtract in the even case and add in the odd case. We have,

$$\left[1 \pm \binom{\sigma+1}{3}\right]\left[f_{jk(\sigma-2)i} \mp f_{ji(\sigma-2)k}\right] - \left[\binom{\sigma}{2} \pm \binom{\sigma-1}{1}\right]\left[\mathrm{M}_{j(\sigma-1)i(\sigma)k} \mp \mathrm{M}_{j(\sigma)i(\sigma-1)k}\right] = 0 \quad (2\cdot11)$$

(Upper sign in the even case.)

The others give us the following equations:

$$\binom{\sigma-2}{p} f_{jk(\sigma-2)i} - \binom{\sigma-1}{p} \mathrm{M}_{j(\sigma-1)i(\sigma)k} + \binom{\sigma}{p} \mathrm{M}_{j(\sigma)i(\sigma-1)k} - \binom{\sigma+1}{p} f_{ji(\sigma-2)k} = 0 \quad (2\cdot12)$$

$$p = 0, 1, \ldots . \sigma-3$$

(2·11) and (2·12) are a set of $(\sigma-1)$ linear homogeneous equations in the 4 unknowns $f_{jk(\sigma-2)i}$, $\mathrm{M}_{j(\sigma-1)i(\sigma)k}$, $\mathrm{M}_{j(\sigma)i(\sigma-1)k}$, $f_{ji(\sigma-2)k}$ and hence they vanish if $\sigma-1 \geqslant 4$ and the matrix of the coefficients is of rank 4. When $\sigma-1 = 4$, we find that the corresponding determinant vanishes. Hence for $\sigma+1 \geqslant 7$ we have

$$f_{ij(\sigma-2)k} = 0,\ \mathrm{M}_{i(\sigma)j(\sigma-1)k} = 0 \quad (2\cdot13)$$

Proceeding thus we arrive at the results:

$$\left.\begin{aligned} f_{ij(\mu)k} &= 0 \qquad \mu > \lambda \\ M_{i(\sigma)j(\mu)k} &= 0 \qquad \mu > \lambda + 1 \\ M_{i(\sigma-1)j(\mu)k} &= 0 \quad \mu > \lambda + 2 \end{aligned}\right\} \qquad (2\cdot14)$$

and so on, where λ has the value given in (1·1).

When $\sigma + 1 = 2\lambda$, we arrive at the critical stage while considering the condition (2·1) for $p = \lambda$. We get

$$\left[f_{ik(\lambda)j} + (-1)^{\lambda+1} f_{jk(\lambda)i} - \binom{2\lambda}{\lambda} f_{ji(\lambda)k}\right]$$
$$= (-1)^{\lambda+1}\binom{\lambda+1}{\lambda} M_{j(\lambda+1)i(\sigma)k} + (-1)^{\lambda+2}\binom{\lambda+2}{\lambda} M_{j(\lambda+2)i(\sigma-1)k} + \cdots$$
$$\cdots + (-1)^{\sigma}\binom{\sigma}{\lambda} M_{j(\sigma)i(\lambda+1)k}.$$

Interchanging i and k and subtracting, we get

$$a_0\,[f_{ik(\lambda)i} - f_{ji(\lambda)k}] + a_1\,[M_{j(\lambda+1)i(\sigma)k} - M_{j(\lambda+1)k(\sigma)i}] + \cdots = 0 \qquad (2\cdot15)$$

Similarly, from the remaining conditions we have

$$\binom{\lambda}{p} f_{ik(\lambda)i} - \binom{\lambda+1}{p} M_{j(\lambda+1)i(\sigma)k} + \binom{\lambda+2}{p} M_{j(\lambda+2)i(\sigma-1)k} - \cdots$$
$$\cdots + (-1)^{\lambda}\binom{2\lambda}{p} f_{ji(\lambda)k} = 0 \qquad (2\cdot16)$$
$$p = 0,\ 1, \ldots\ldots \lambda - 1.$$

(2·15) and (2·16) together are a set of $(\lambda + 1)$ equations in the $(\lambda + 1)$ unknowns $f_{jk(\lambda)i}$, $f_{ji(\lambda)k}$, $M_{j(\lambda+1)i(\sigma)k}$, $M_{j(\lambda+2)i(\sigma-1)k} \cdots M_{j(\sigma)i(\lambda+1)k}$.

But the determinant of the coefficients is of *rank* λ. Hence the quantities do not vanish and there is a unique solution for their ratios. The determinant in question is

$$\begin{vmatrix} a_0 & a_1 & a_2 & \cdots & a_\lambda \\ \binom{\lambda}{0} & -\binom{\lambda+1}{0} & \binom{\lambda+2}{0} & \cdots & (-1)^{\lambda}\binom{2\lambda}{0} \\ \binom{\lambda}{1} & -\binom{\lambda+1}{1} & \binom{\lambda+2}{1} & \cdots & (-1)^{\lambda}\binom{2\lambda}{1} \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \binom{\lambda}{\lambda-1} & -\binom{\lambda+1}{\lambda-1} & \binom{\lambda+2}{\lambda-1} & \cdots & (-1)^{\lambda}\binom{2\lambda}{\lambda-1} \end{vmatrix}$$

where $a_p + a_q = 0$ if $p + q = \lambda$.

For convenience let us consider the determinant

$$\begin{vmatrix} \beta_0 & \beta_1 & \cdots & \beta_\lambda \\ \binom{\lambda}{0} & \binom{\lambda+1}{0} & \cdots & \binom{2\lambda}{0} \\ \binom{\lambda}{1} & \binom{\lambda+1}{1} & \cdots & \binom{2\lambda}{1} \\ \cdots & \cdots & \cdots & \cdots \\ \binom{\lambda}{\lambda-1} & \binom{\lambda+1}{\lambda-1} & \cdots & \binom{2\lambda}{\lambda-1} \end{vmatrix}$$

so that $\beta_r = (-1)^r \alpha_r$.

Let us keep the first column as it is, and subtract from each one of the remaining columns, the previous column and use the formula $\binom{n}{r} - \binom{n-1}{r} = \binom{n-1}{r-1}$. Repeat the process, stopping at the second row, then at the third row and so on. Finally after λ such operations, the matrix of the binomial coefficients alone will become

$$\begin{vmatrix} \binom{\lambda}{0} & 0 & 0 & \cdots & 0 & 0 \\ \binom{\lambda}{1} & \binom{\lambda}{0} & 0 & \cdots & 0 & 0 \\ \binom{\lambda}{2} & \binom{\lambda}{1} & \binom{\lambda}{0} & \cdots & 0 & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \binom{\lambda}{\lambda-1} & \binom{\lambda}{\lambda-2} & \binom{\lambda}{\lambda-3} & \cdots & \binom{\lambda}{0} & 0 \end{vmatrix}$$

There are λ rows and $(\lambda + 1)$ columns.

As a result of these operations which are merely taking the successive finite differences, the last element in the first row of the β's will become

$$\beta_\lambda - \binom{\lambda}{1}\beta_{\lambda-1} + \binom{\lambda}{2}\beta_{\lambda-2} \cdots + (-1)^\lambda \binom{\lambda}{\lambda}\beta_0$$

and

$$\beta_r = (-1)^r \alpha_r$$

$\therefore$ This is equal to

$$a_\lambda + \binom{\lambda}{1} a_{\lambda-1} + \binom{\lambda}{2} a_{\lambda-2} + \cdots + \binom{\lambda}{\lambda} a_0$$

with the proper sign.

As $a_p + a_q = 0$ when $p + q = \lambda$, this expression vanishes.

So all the elements of the last column in the determinant are zero and hence the determinant vanishes.*

Also it is seen from the above that the determinant of order λ formed by the binomial coefficients is equal to 1.

The $(\lambda + 1)$ quantities $f_{jk(\lambda)i}$, $M_{j(\lambda+1)i(\sigma)k}$, $\ldots$. $M_{j(\sigma)i(\lambda+1)k}$, $f_{ji(\lambda)k}$ are hence proportional to $A_0, A_1, \ldots . A_\lambda$, the co-factors of $a_0, a_1, \ldots . a_\lambda$ in the determinant. It is seen that $A_r = \binom{\lambda}{r}$.

This proves that

$$\left.\begin{aligned} f_{jk(\lambda)i} &= f_{ji(\lambda)k} \\ M_{i(\lambda+1)j(\sigma)k} &= M_{i(\sigma)j(\lambda+1)k} \end{aligned}\right\} \quad (2\cdot17)$$

and so on.

Also

$$\frac{f_{ij(\lambda)k}}{\binom{\lambda}{0}} = \frac{M_{i(\lambda+1)j(\sigma)k}}{\binom{\lambda}{1}} = \frac{M_{i(\lambda+2)j(\sigma-1)k}}{\binom{\lambda}{2}} = \ldots .$$

The symmetry of f_{ij} together with the first of conditions (2·17) ensures that

$$f_{ij} = f_{(\lambda)i(\lambda)j} \quad (2\cdot18)$$

When $(\sigma + 1) = 2\lambda + 1$ we have the following equations corresponding to (2·15) and (2·16).

$$\left[f_{ik(\lambda)j} + (-1)^{\lambda+1} f_{jk(\lambda)i} + \binom{2\lambda+1}{\lambda} f_{ji(\lambda)k}\right]$$
$$= (-1)^{\lambda+1}\binom{\lambda+1}{\lambda} M_{j(\lambda+1)i(2\lambda)k} + (-1)^{\lambda+2}\binom{\lambda+2}{\lambda} M_{j(\lambda+2)i(2\lambda-1)k} +$$
$$\ldots . + (-1)^{\sigma}\binom{2\lambda}{\lambda} M_{j(2\lambda)i(\lambda+1)k}. \quad (2\cdot19)$$

and

$$\binom{\lambda}{p} f_{jk(\lambda)i} - \binom{\lambda+1}{p} M_{j(\lambda+1)i(\sigma)k} + \ldots . + (-1)^{\lambda+} \binom{2\lambda+1}{p} f_{ji(\lambda)k} = 0$$
$$p = 0, 1, \ldots . . \lambda - 1. \quad (2\cdot20)$$

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* I am thankful to Mr. M. Venkatraman in helping me to evaluate this determinant.

These are $(\lambda + 1)$ equations in $(\lambda + 2)$ unknowns. Let us permute i, j, k cyclically twice and add. Let

$$A_{[ijk]} \equiv (A_{ijk} + A_{jki} + A_{kij}).$$

We get, then $(\lambda + 1)$ equations in the $(\lambda + 1)$ unknowns

$$f_{[ij(\lambda)k]},\ M_{[i(\lambda+1)j(2\lambda)k]},\ \ldots\ldots,\ M_{[i(2\lambda)j(\lambda+1)k]}$$

The determinant of the coefficients can by the methods followed in the symmetric case, be shown to be *not* equal to zero.

Hence

$$f_{ij(\lambda)k} + f_{jk(\lambda)i} + f_{ki(\lambda)j} = 0 \tag{2·21}$$

This, together with the anti-symmetry of f_{ij}, ensures that f_{ij} is a curl, *i.e.*,

$$f_{ij} = \phi_{i(\lambda)j} - \phi_{j(\lambda)i}. \tag{2·22}$$

By equating to zero, the residual terms in the above conditions for different values of p we get conditions on the various curvature tensors.

For $p = \sigma$ we get $D f_{ij} = 0$

For $p = \sigma - 1$ we will have

$$f_{ir} \underset{\sigma-1}{P^r_j} = (-1)^{\sigma-1} f_{jr} \underset{\sigma-1}{P^r_i}$$

and so on, for the general p,

$$f_{ir} \underset{p}{P^r_j} = f_{jr} \sum_{s=p}^{\sigma-1} (-1)^s \binom{s}{p} D^{s-p} \underset{s}{P^r_i}. \tag{2·23}$$

From (2·14) we infer that the Euler equations should be of the form

$$f_{ij}(x^{(\sigma+1)i} + \alpha^i) \equiv f_{ij}(\lambda)\, x^{(\sigma+1)i} + a_{ij}(\lambda + 1)\, x^{(\sigma)i} + \\ + b_{ij}(\lambda + 2)\, x^{(\sigma-1)i} + \tag{2·24}$$

where

$f_{ij}(\lambda)$ means that f_{ij} contains $x,\ x', \ldots . x^{(\lambda)}$.

The terms are linear up to $x^{(m)i}$ where $m = I\left(\frac{3\lambda}{2} + 1\right)$.

3. *Conditions of Integrability.*—The conditions of self-adjoincy of the variation of Hi, we have seen are,

$$H_{i(p)j} = \sum_{r=p}^{\sigma+1} (-1)^r \binom{r}{p} H^{(r-p)}_{j(r)i}.$$

The right-hand side resembles the E-vectors of Synge. Let us express this in invariant form making use of the identities in the present author's previous paper.[5] We get

$$\begin{aligned}
&\underset{p}{\nabla_j} H_i - \sum_{\gamma=p+2}^{\sigma+1} \underset{\gamma}{\nabla_l} H_i \left[\sum_{r=0}^{\gamma-p-2} (-1)^{r+1} \binom{\sigma-\nu+r}{r} D^r P^l_{\sigma-\gamma+p+r+1} \right] \\
&= \sum_{\gamma=p}^{\sigma+1} (-1)^\gamma \binom{\nu}{p} D^{\nu-p} \underset{\nu}{\nabla_i} H_j \\
&+ \sum_{\gamma=1}^{\sigma-p} \left[\left\{ \sum_{s=0}^{\nu-1} (-1)^s \binom{\sigma-\nu+s}{s} D^s P^l_{i\,\sigma-\nu+s} \right\} \times \right. \\
&\qquad \left. \left\{ \sum_{r=0}^{\sigma-\nu} (-1)^r \binom{r}{p} D^{r-p} \underset{r+\nu+1}{\nabla_l} H_j \right\} \right]
\end{aligned}$$

We can re-write this in the form

$$\begin{aligned}
&\underset{p}{\nabla_j} H_i - \sum_{\nu=p+2}^{\sigma} \underset{\nu}{\nabla_l} H_i \left[\sum_{r=0}^{\nu-p-2} (-1)^{r+1} \binom{\sigma-\nu+r}{r} D^r P^l_{j\,\sigma-\nu+p+r+1} \right] \\
&- \sum_{\nu=p}^{\sigma} (-1)^\nu \binom{\nu}{p} D^{\nu-p} \underset{\nu}{\nabla_i} H_j \\
&- \sum_{\nu=1}^{\sigma-p} \left[\left\{ \sum_{s=0}^{\nu-1} (-1)^s \binom{\sigma-\nu+s}{s} D^s P^{li}_{\sigma-\nu+s} \right\} \right. \\
&\qquad \left. \times \left\{ \sum_{r=0}^{\sigma-\nu-1} (-1)^r \binom{r}{p} D^{r-p} \underset{r+\nu+1}{\nabla_l} H_j \right\} \right] \\
&= - \underset{\sigma+1}{\nabla_l} H_i \left\{ P^l_{j\,p} \right\} + \underset{\sigma+1}{\nabla_l} H_j \left\{ \sum_{s=0}^{\sigma-p-1} (-1)^{p+s} \binom{p+s}{s} D^s P^l_{i\,p+s} \right\} \\
&+ (-1)^{\sigma+1} \binom{\sigma+1}{p} D^{\sigma+1-p} \underset{\sigma+1}{\nabla_i} H_j \\
&+ \sum_{\nu=1}^{\sigma-p-1} \left[\left\{ \sum_{s=0}^{\nu-1} (-1)^s \binom{\sigma-\nu+s}{s} D^s P^l_{i\,\sigma-\nu+s} \right\} \times \right. \\
&\qquad \left. \times \left\{ (-1)^{\sigma-\nu} \binom{\sigma-\nu}{p} D^{\sigma-\nu+p} \underset{\sigma+1}{\nabla_l} H_j \right\} \right] \\
&\qquad p = 0, 1, \ldots \sigma. \qquad (3\cdot1)
\end{aligned}$$

The left side of (3·1) equated to zero give us the self-adjoincy conditions for equations of order σ. We have to show that they are satisfied by $H_i \equiv \delta_i f$.

Since f is known, we see that

$$\delta_i f = f_{ij}\, x^{(\sigma+1)j} + A_i(\sigma)$$

and hence

$$\underset{\sigma+1}{\nabla_j} (\delta_i f) = f_{ij}.$$

[5] V. Seetharaman, *Proc. Lond. Math. Soc.*, 1939, Series 2, **45**, formula (3·7).

The right side of (3·1) consequently becomes

$$= \left[-f_{ir} \mathrm{P}^{r}_{p\ j} + f_{jr} \sum_{s=p}^{\sigma-1} (-1)^s \binom{s}{p} \mathrm{D}^{s-p} \mathrm{P}^{r}_{s\ i} \right]$$

$$+ (-1)^{\sigma+1} \binom{\sigma+1}{p} \mathrm{D}^{\sigma+1-p} f_{ji}$$

$$+ \sum_{\nu=1}^{\sigma-p-1} \left[\left\{ \sum_{s=0}^{\nu-1} (-1)^s \binom{\sigma-\nu+s}{s} \mathrm{D}^s \mathrm{P}^{j}_{\sigma-\nu+s\ i} \right\} \times \right.$$

$$\left. \times \left\{ (-1)^{\sigma-\nu} \binom{\sigma-\nu}{p} \mathrm{D}^{\sigma-\nu+p} f_{jl} \right\} \right] \qquad (3\cdot2)$$

These equated to zero are the self-adjoincy conditions for the equations of order $(\sigma + 1)$.[6] Hence we have established the conditions of Integrability and hence the main theorem of this note.

[6] *Vide* formulæ (2·7) and (2·23). Also *cf.* D. D. Kosambi, *Quart. J. of Math.*, 1936, 7, 104.

SEPARATION OF ELECTRONIC AND NON-ELECTRONIC COMPONENTS OF COSMIC RADIATION BY BHABHA'S METHOD

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Introduction

Whenever the intensity of the hard component of cosmic radiation is measured, the soft component is usually cut out by the inclusion of an absorber like lead between the counters of a counter telescope. If small thicknesses of lead are used for the purpose, all the electrons cannot be absorbed. If large thicknesses of lead are used, there is always the possibility of cutting out low energy mesons. Schein, Jesse and Wollan[1] and Sarabhai[2] have made use of the fact that electrons produce showers to cut out electrons. Bhabha[3] has considered this problem in detail and has arrived at certain conclusions on the basis of the cascade theory. He has shown that any given thickness of lead can be made more effective in cutting out electrons by splitting it in the approximate ratio of 1 : 4. The smaller thickness is to be used for shower production and the high energy electrons get cut out by the showers tripping counters in anti-coincidence included in the counter telescope. A fraction of low energy electrons produce showers of very few particles, often of only one, in the shower producing lead. This fraction is quite large and can only be cut out by absorption in the larger block of lead. Experiments were carried out by the author to test these conclusions of Bhabha at Ootacamund (Geomagnetic latitude = 1·7° N. and altitude = 7,200 ft. above mean sea-level) and this paper is mainly a report of that work. In particular, the theoretical result is confirmed that shower production alone is not sufficient to cut out the whole electronic component, and the lower block of lead is essential for the purpose of cutting out the relatively lower energy electrons.

Experimental Arrangement

In designing the apparatus, the choice of the total thickness of lead to be used was of primary importance. A total thickness of 5·25 cm. was used and the reason for choosing this thickness is as follows. Bhabha has shown that this thickness cuts out all but about 5% of the electrons and that splitting the lead would only assist in cutting out this last 5%. According to Rossi and Greisen,[4] mesons of energy above $0{\cdot}93 \times 10^8$ eV can penetrate 5·25 cm. of lead. From the curve given by Euler and Heisenberg[5] for the

energy spectrum of mesons, the fraction of mesons of energy below 10^8 eV is about 2% of the total meson intensity. It is clear therefore that very few mesons would be absorbed in this thickness of 5·25 cm. Of this, 1·25 cm. were used for shower production and 4·0 cm. for absorption only. The number of mesons cut out by shower production in 1·25 cm. of lead is quite negligible.

The counter telescope used for the experiments is shown in Fig. 1. Counters 1, 2 and 3 form the vertical telescope and they can all be connected in coincidence. Counters 4 and 5 are connected in parallel and can be set in anti-coincidence with counters 1, 2 and 3. The pulse was taken from the copper cylinders of the anti-counters and they were enclosed in an earthed shield of 1/32″ aluminium. All the counters used were of the same size, *viz.*, 6″ long and 1¼″ in diameter.

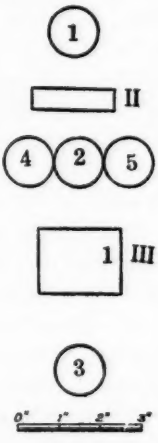

FIG. 1

Each of the counters, 1, 2 and 3, was fixed in two duraluminium rings 1/16″ thick and ¼″ wide. These rings were rivetted to a rectangular frame of the same thickness and width. This frame was fixed at the two ends to two L angles which acted as vertical supports. The frames in positions II and III for supporting lead consisted of a rectangular frame similar to the ones used for the counters but had cross strips instead of the rings. The shields of counters 4 and 5 were attached to the rectangular frame of counter 2. The complete structure weighed only 4 ozs. This gives an idea of the extent to which showers, etc., caused in the frame are reduced to a minimum. This kind of frame also enabled the alignment of counters to be done with a high degree of precision.

Location of the Apparatus

The counter telescope was first placed in open air with no lead in positions II and III. Counters 1, 2 and 3 were connected in coincidence and counts registered for 8 hours. The reading was 1531, giving an hourly average of $191·4 \pm 3·3$. Next the apparatus was shifted to a large room having a thin roof of tile and the experiment was repeated. 4579 counts were registered in 24 hours. This gives an hourly average of $190·8 \pm 1·9$. Since the two readings were substantially the same, all other measurements were carried out inside the room.

Effect of Side Showers

It has recently been pointed out[6] that errors due to chance coincidences, inefficiency of counters, etc., are negligible in coincidence counter work when

compared with the errors due to the effect of side showers. Consequently it was felt desirable to obtain some information on the effect of side showers before actually commencing measurements. The observations recorded for the purpose are given below in Table I.

TABLE I

(*No lead is placed in positions II or III*)

No.	Counters in coincidence	Counters in anti-coincidence	Counts	Time	Counts/hour	% effect of showers
a	123	..	4579	24	190·8 ±1·9	4·4
b	123	45	8768	48	182·7 ±1·3	..
c	13	..	1688	7·5	225·1 ±3·7	23·2
d	13	45	1940	9	215·6 ±3·3	18·0

One method of estimating the effect of side showers on a counter telescope is to put one of the counters out of line. In (*b*), two counters 4 and 5 are out of line and in anti-coincidence with counters 1, 2 and 3. Therefore, the arrangement (*b*) can be considered to give the readings free from the effect of side showers. The only objection to this is the fact that it cuts out a certain number of Auger showers. But since the difference between (*a*) and (*b*) is only 4·4%, it is clear that the number of Auger showers ruled out by this method is certainly less than 4·4%.

The percentage effect of side showers calculated on the assumption that (*b*) gives the correct reading is shewn in the last column.

Results of Measurements

Counters 1, 2 and 3 were connected in coincidence. Counters 4 and 5 were connected in parallel and in anti-coincidence with counters 1, 2 and 3. The distance of the tray of counters 4, 2 and 5 from the shower producing lead in position II is rather *critical*. The position shown in the figure was best and has, therefore, been used. As it was found that there was a distinct diurnal variation of meson intensity, all measurements were taken for periods of 24 hours at a time. Owing to unavoidable reasons, the last measurement in Table II could only be taken for 10 hours. Each of the measure-

TABLE II

No.	Lead in position II	Lead in position III	Counts	Time	Counts/hour
	cm.	cm.			
A	..	..	4389+4379	24+24	182 ±1·3
B	1·25	4·0	2889+2924+2902+2911	24+24+24+24	121·1 ±0·75
C	..	5·25	3008+3010	24+24	125·4 ±1·08
D	1·25	..	3336	24	139·0 ±1·6
E	..	1·25	1485	10	148·5 ±2·6

ments for 24 hours periods were taken at random and the consistency gave an independent check on the efficiency, etc., of the counters and circuits. The readings obtained for each period of 24 hours are shown separately in the table.

Discussion of the Results

(A) gives the total intensity and (B), on the basis of Bhabha's theory, the intensity of the hard component. (A−B) gives the total electron component. (C−B) represents the number of electrons which can penetrate 5·25 cm. of lead but which can be cut out by splitting the lead as suggested by Bhabha. $(C-B)/(A-B) \times 100 = 7{\cdot}0 \pm 2{\cdot}9\%$. According to Bhabha, about 5% of the total electron component can penetrate 5·25 cm. of lead and this can be cut out by splitting the lead. Therefore, the experimental result, *viz.*, $7{\cdot}0 \pm 2{\cdot}9\%$ is in agreement with Bhabha's calculations.

(D) gives the result of using only the shower producing lead. It is clear that a considerable number of electrons get through. This number is obtained by subtracting (B) from (D). It is found to be 29·1% of the total electron component. The necessity for using the extra 4·0 cms. of lead for *absorption only*, therefore, becomes obvious and is in accordance with Bhabha's deductions.

(A−E) represents the electron component absorbed in 1·25 cm. of lead.

As it is possible to get some idea of the energy spectrum of electrons from these experiments, the results are tabulated below in a slightly different manner and are of some significance as the measurements were carried out very near the geomagnetic equator (1·7° N) and at a high altitude (7,200 ft.).

TABLE III

Component	How deduced	Intensity in counts/hour	% of total soft component
1. Very low energy electrons absorbed in 1·25 cm. of lead	(A−E)	34·2	55·5
2. Low energy electrons absorbed in 5·25 cm. of lead which penetrate 1·25 cm. but are incapable of producing showers in 1·25 cm. of lead to trip counters 4 or 5	(D−B)	17·9	29·1
3. High energy electrons absorbed in 5·25 cm. of lead but capable of producing showers in 1·25 cm. of lead to trip counters 4 or 5	{(E−D)−(C−B)}	5·2	8·4
4. Very high energy electrons capable of penetrating 5·25 cm. of lead	(C−B)	4·3	7·0
5. Electrons absorbed in 5·25 cm. of lead	(A−C)	57·3	93·0

The total intensity and the percentages of the soft and hard components are given below:—

TABLE IV

Component	How deduced	Intensity in counts/hour	% of total intensity
Total intensity	A	182·7	..
Hard component	B	121·1	66·3
Soft component	A—B	61·6	33·7

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Summary

The theoretical results of the method suggested by Bhabha for the separation of the electronic and non-electronic components of cosmic radiation are experimentally verified. The absorption spectrum of electrons has been investigated by this method. At 1·7° N. of the geomagnetic equator and an altitude of 7,200 ft., the hard component constitutes 66·3% of the total intensity.

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THE EVALUATION OF THE SPECIFIC HEAT OF ROCK-SALT BY THE NEW CRYSTAL DYNAMICS

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1. Introduction

Rock-salt is a typical polar crystal and has therefore been a subject of close study by many theoretical physicists. Numerous attempts have been made to correlate its observed properties with the forces operative in its structure. A simplified method of treatment was first given by Madelung (1910) and later by Born and Karman (1912) in which the actual forces were replaced by quasi-elastic bindings between the neighbours and next nearest neighbours, and a determination of the infra-red frequencies was attempted from Voigt's elastic constants. The approximation used was obviously unsatisfactory because the forces between the ions are electrical in nature and are not confined to the neighbouring atoms alone but in consequence of Coulomb's Law, diminish very slowly with the distance. The ionic theory of crystals developed by Born and his school takes the electrical origin of the forces into consideration and has, at present, reached a finished state in which it has been possible to determine the various observed properties of polar crystals such as lattice energy, lattice constant, compressibility, etc., from the forces between the ions. Amongst the more recent workers who have made such calculations successfully are Huggins (1937) and Wasestjerna (1939). In their application to the problem of lattice vibrations and specific heats, it has been customary to proceed on the basis of the lattice theory of Born and Karman which gives a continuous spectrum of frequencies in the optical branch. A few typical frequencies corresponding to some important normal modes are usually evaluated and an estimate made of the approximate form of the Born and Karman frequency distribution curve. For NaCl, this has been partially done by Lyddane and Herzfeld (1938) who have given the numerical values of a few frequencies. Kellermann (1940) has determined a larger number (288) and has, in addition, used them for evaluation of the specific heats (1941).

Spectroscopic studies, however, show that the vibrations of crystal lattices exhibit numerous discrete frequencies, and do not support the theory

of Born and Karman which demands a continuous spectrum for them. In the case of diamond, for example, the experimental situation in this respect has been made perfectly clear by several independent methods of investigation, *viz.*, the study of the luminescence, absorption, and Raman spectra [Nayar, 1941–42; Miss Mani (under publication); R. S. Krishnan (under publication]. That a similar situation arises also in the case of rock-salt is apparent from Rasetti's photographs of its Raman spectrum (Rasetti, 1931; Fermi, 1938), the interpretation of which on the basis of the selection rules has been discussed by R. S. Krishnan (1943). In order to explain these experimental facts, Sir C. V. Raman (1943) has recently made a new approach to the whole problem of lattice vibrations. According to his theory, the vibration pattern of the optical spectrum repeats itself exactly in a supercell consisting of eight simple cells. The normal modes of the lattice can then be described in terms of those of this supercell. For a face-centred cubic lattice the supercell has, besides the three translations, four modes of oscillation corresponding respectively to the cases when the atoms in successive octahedral or cubic planes move with opposite phases and either transversely or longitudinally to these planes. In rock-salt which consists of two interpenetrating face-centred lattices, we have double the number, namely eight modes, in addition to the fundamental vibration of the structure in which Cl and Na lattices vibrate against each other as a whole. There are thus nine optical modes which comprise 45 out of a total of 48 degrees of freedom, the remaining three degrees going over to the elastic spectrum. Chelam (1943) has given a description of the nine modes with the degeneracies attached to each of them. The numerical values of the corresponding frequencies can be easily obtained either from Lyddane and Herzfeld's work (*l.c.*) or Kellermann's (*l.c.*), and with the help of the known degeneracies it is possible to calculate the specific heats of the crystal and to compare them with the thermal data.

2. *Evaluation of the Frequencies*

(*a*) *Optical Frequencies.*—The nine possible modes of vibration of the lattice have been reproduced from Chelam's paper along with their degeneracies in Table I, which also contains the numerical values of corresponding frequencies as calculated by Lyddane and Herzfeld and by Kellermann. For comparison we have also given the frequencies derived by R. S. Krishnan from the observed lines in Rasetti's photographs of Raman effect on the basis (suggested by the selection rules) that they represent the octaves of the fundamental lattice oscillations. The values given in the last column are, therefore, half of the observed frequencies. It will be seen that seven of the calculated frequencies agree closely with the experimental values, the

TABLE I

Lattice Frequencies of Rock-salt

Designation and Description of Mode	Degeneracy	Calculated Frequency I	Calculated Frequency II	Observed Frequency
		Cm.$^{-1}$	Cm.$^{-1}$	Cm.$^{-1}$
ν_1 : Oscillation of sodium and chlorine lattices against each other ..	3	162	152	158
ν_2 : Oscillation of sodium layers against each other normally to the octahedral planes	4	244	240	..
ν_3 : Oscillation of chlorine layers against each other normally to the octahedral planes	4	196	193	175
ν_4 : Same as ν_1 but transversely ..	8	135	127	140
ν_5 : Same as ν_3 but transversely ..	8	109	102	117
ν_6 : Coupled oscillation of sodium and & chlorine ions normally to the cubic	3	226	223	..
ν_7 : planes	3	170	165	170
ν_8 : Coupled oscillation of sodium and & chlorine ions tangentially to the cube	6	173	164	170
ν_9 : planes	6	99	94	91

I from Lyddane and Herzfeld (*loc. cit.*, p. 858) ; II from Kellermann (*loc. cit.*, p. 543).

agreement with the results of Lyddane and Herzfeld being slightly better. The slight difference between the two calculated values arises from the fact that the authors have used slightly different constants for the repulsive forces (A and B of Kellermann's paper). For the infra-red proper frequency 162 cm.$^{-1}$ which corresponds to the vibration of the Na and Cl lattices against each other, Lyddane and Herzfeld have got the curious result that the frequencies of longitudinal and transverse oscillations are different from each other. Kellermann has questioned the validity of this result, and has obtained the same frequency for both the types, thus confirming the triple degeneracy assigned to this vibration by Chelam. Kellermann's expression for this frequency is the same as that of the transverse frequency of the former authors, the difference in numerical values again arising from the choice of slightly different constants. For this reason, we have only given the transverse frequency of Lyddane and Herzfeld in column III.

(*b*) *Elastic Spectrum.*—We have now to determine the frequency spectrum corresponding to the three degrees of freedom left over after the enumeration of the optical modes of vibration. We have no spectroscopic data which would enable us to do this. On the other hand, a theoretical calculation of the nature of this spectrum would involve much labour and would also raise difficult questions as to the possible influence of the external boundary of the crystal on the modes of vibration other than those

considered above. For these reasons, it is both convenient and probably also a fair approximation to the truth to identify the three omitted degrees of freedom with the elastic spectrum of the solid and to calculate its contribution to the thermal energy by means of a Debye function, the characteristic temperature θ_D being obtained from the elastic data. It is usual to do this using the formula

$$\theta_D = \frac{h}{k}\left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}} \bar{v}$$

where V is the atomic volume, and $\bar{v}$ is obtained from

$$\frac{1}{\bar{v}^3} = \frac{1}{3}\sum_1^3 \frac{1}{4\pi}\int\int \frac{1}{v_i^3}\, d\omega$$

v_i is the velocity of elastic waves in the direction i and the summation is over all the three waves for the whole solid angle. The integral (2) has been evaluated by Durand (1936) by Hopf and Lechner's interpolation method from the elastic constants at 80° K. The numerical value of θ_D is 320° K. In Raman's theory, only 1/16 of the total degrees of freedom in the rock-salt structure are assignable to the elastic spectrum. The formula for the characteristic temperature has therefore to be modified by writing $\frac{3N}{16}$ in place of 3N. We thus obtain

$$\theta_D = \frac{320}{\sqrt[3]{16}} = 127° \text{ K.}$$

3. *Evaluation of* C_v

Unfortunately, the experimental data on the molar heats of rock-salt are very meagre. Nernst (1911) measured the specific heats at a few temperatures from 25° to 238° K, and these are practically the only data available to us. Mcgraw's (1931) measurements cover a large number of temperatures between 95 and 245° K, and show a maximum deviation of 5% from Nernst's results, but he himself considers Nernst's values as more reliable. As a matter of fact, his measurements were made to test the accuracy of his technique by comparing his results with those of Nernst. Clusius, Perlick and Goldmann's (Keesom, 1934) measurements extend only to a small range between 10 and 40° K. Their experimental results have not been reported, but a θ_D/T curve has been given in the above-mentioned paper. This is rather unfortunate since a 1% deviation from θ_D/T curve in this region corresponds to a 3% error in the specific heats. The experimental values between 10 and 40° K in the last column of Table II have been read from the above curve, at 25° and 28° K by us, and at other temperatures by Blackman (1942). Nernst's values wherever available have been shown in the last column but

one. They have been taken from *Handbuch der Experimental Physik*, vol. 8 page 256, which contains the values of C_v. It will be noticed that there is a large difference of the order of 10 to 15% between the two sets of observations.

For the purpose of evaluation of C_v we have preferred to use Lyddane and Herzfeld's values of the frequencies, as they seem to be nearer to the experimental values both in the infra-red and the Raman effect. That Kellermann's values are definitely lower is also seen from the fact that his elastic constants (c_{11} and c_{12}) are slightly smaller than the observed ones. Of course, considering the nearness of the two sets of frequencies and the large uncertainty in the experimental values of C_v, this particular choice is not very material. The expression for C_v (Molar) is

$$C_v \text{ (molar)} = 3R\left[\sum_1^9 \sigma_s \, E\left(\frac{h\nu_s}{kT}\right) + \frac{1}{8} D\left(\frac{127}{T}\right)\right],$$

where E and D stand for the Einstein and Debye functions respectively, and σ_s is the statistical weight of the frequency ν_s and has the value $\frac{1}{8}$, $\frac{1}{6}$, $\frac{1}{6}$, $\frac{1}{3}$, $\frac{1}{3}$, $\frac{1}{8}$, $\frac{1}{8}$, $\frac{1}{4}$ and $\frac{1}{4}$ for each of the frequencies of Table I taken in order. The results of the calculations are shown in Table II. They exhibit a very close agreement with Perlick's observations wherever they are available.

TABLE II

Molecular Heats of NaCl

Temperature °K	Optical frequencies	Elastic Spectrum	Total C_v	C_v Experimental (Nernst)	C_v Experimental C, P & G
10	..	·0282	·0282	..	·0326
20	·123	·176	·299	..	·310
25	·379	·268	·65	·58	·63
28	·602	·319	·92	·80	·93
30	·794	·350	1·14	..	1·150
40	1·911	·471	2·38	..	2·380
69	5·204	·633	5·84	6·24	..
81·4	6·26	·66	6·92	7·04	..
83·4	6·429	·666	7·10	7·44	..
110	7·964	·698	8·66	8·65*	..
138	8·940	·714	9·65	9·58	..
235	10·30	·73	11·03	11·10	..

* Interpolated by Forsterling (1920) from Nernst's data.

The slight difference at 10° K is probably due to the Debye function not being a very good approximation to the true spectrum. Nernst's values in this region differ considerably from those of the other investigators, and at 83·4° show rather too large an increase for a rise of 2°. Considering

these facts, the agreement with Nernst's results at the higher temperatures seems to be quite satisfactory.

In conclusion, the author wishes to record his grateful thanks to Professor Sir C. V. Raman for the interest taken by him in this work.

4. *Summary*

The new treatment of the dynamics of crystal lattices put forward by Sir C. V. Raman shows that the rock-salt structure has nine distinct frequencies of vibration in the optical branch which represent forty-five out of the forty-eight degrees of freedom of the group of 8 sodium and 8 chlorine ions present in a super-lattice cell. The theoretical calculations of Lyddane and Herzfeld as well as those of Kellermann have enabled these nine frequencies to be evaluated. They agree well with the experimental frequencies given by Rasetti's photographs of the Raman spectrum. The remaining three degrees of freedom represent the spectrum of the elastic vibrations of the lattice which may be evaluated from the known elastic constants. The thermal energy calculated on this basis shows a very satisfactory agreement with the experimental data.

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